Activity-based fate modelling for risk assessment of three ionizable organic compounds (triclosan, furosemide, ciprofloxacin)

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IWA-11677: Activity-based fate modelling for risk assessment of three ionizable organic compounds (triclosan, furosemide, ciprofloxacin)

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Abstract. In this study, we present an environmental risk assessment (ERA) of three ionizable chemicals (triclosan, furosemide and ciprofloxacin) based on the application of the European REACH (Registration, Evaluation, Authorization and restriction for Chemicals) protocol to real scenarios with reported emissions. Estimation of local and regional predicted environmental concentrations (PECs) in four geographical scenarios with known consumption/in-sewer discharge data (Denmark, Lower Saxony, Southern Sweden, Northern Italy) was performed. Two steady-state, activity-based fate models, SimpleTreat Activity and Multimedia Activity Model for Ionizable Compounds (MAMI) were used for modelling the fate of ionizable compounds based on quantitative structure-activity relationship (QSAR) properties in a wastewater treatment plant (WWTP) and at regional level, respectively. Validation of the two models by comparison of PECs with MECs (measured environmental concentrations) proved to be satisfactory. PECs were finally compared with PNECs (predicted non effect concentrations) in different environmental compartments for risk characterization purposes. Results showed potential risk in freshwater and soil for triclosan and ciprofloxacin.

Introduction and Methods. Ionizable chemicals are approximately half (49%) of all substances registered according to the REACH regulation, issued by the European Union in 2006 [1]. The available tools for the prediction of the environmental fate of chemicals had not been developed for ionizable chemicals, thus novel activity-based models were recently developed and tested ([2], [3]). In this study, we developed extensions to two steady-state activity-based models to predict the fate of three compounds, i.e. triclosan (monovalent acid), furosemide (bivalent acid) and ciprofloxacin (zwitterion), at local and regional level. The study relies on QSAR properties and mass loads entering the modeled systems. Applicability of the models, originally developed for monovalent chemicals ([3]), was extended to bivalent and zwitterionic chemicals, this being achieved by developing an empirical submodel, instead of using $\log K_{ow}$-based regressions, to estimate values of solid-liquid partitioning coefficient, K_d. Thus, a database of K_d measurements at different pH values was derived from literature ([4]). First, fate at local level, i.e. in sewage treatment plants, was assessed by the SimpleTreat Activity model [2], a modification of the conventional SimpleTreat model [5]. This model estimated removal rates by partitioning to primary and secondary sludge and biodegradation in an aeration tank. A second model, the Multimedia Activity Model for Ionizable Compounds (MAMI) [3] (derived from the EUSES SimpleBox model [6]) was used to evaluate fate at regional level, estimating compounds' distribution in eight compartments (air, natural soil, agricultural soil, other soil, freshwater, freshwater sediment, seawater and seawater sediment) of a 40,000 km^2 region. Mass loads of the chemicals locally released via effluent and sludge, as estimated by SimpleTreat Activity, were used as input to the freshwater and agricultural soil compartments, respectively, in MAMI (Fig. 1). Combination of the two models allowed for an estimation of predicted environmental concentrations (PECs) at local and regional level, starting from consumption or WWTP inlet literature data (e.g., [7]). Thus, the procedure served for an environmental risk assessment of the three chemicals in specific geographical scenarios: Lower Saxony (2002), Denmark (2010), and Southern Sweden (1999) for triclosan; Northern Italy (1997, 2001, 2006) and Denmark (1997) for furosemide; Northern Italy for ciprofloxacin (2006). Obtained PECs of the chemicals were compared to published (i) measured concentrations (MECs) for the purpose of models' validation ([8], [9], [10], [11]); and (ii) PNEC values (e.g., for triclosan [12], [13]) aiming for the calculation of risk quotients, i.e. PEC/PNEC ratios.

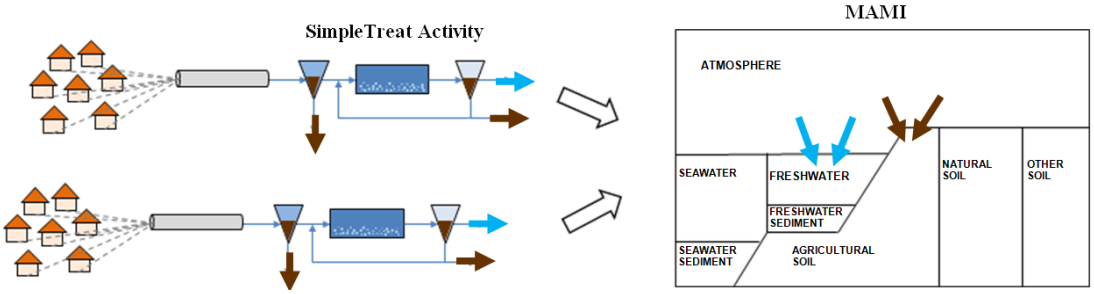

Figure 1. Flow scheme of the model combination for risk assessment of ionizable chemicals. Starting from consumption and/or in-sewer release data, fate in WWTPs (SimpleTreat Activity) and at regional level (MAMI) was assessed. Loads released via sewage effluent and sludge were used as input to MAMI in freshwater and agricultural soil compartments, respectively.

Results and discussion. Estimations from SimpleTreat Activity showed that: (i) 48% of influent triclosan load was biotransformed (median of the scenarios) and 27% sorbed to primary and secondary sludge; (ii) furosemide was mostly released undegraded via effluent (65%), without sorption; (iii) ciprofloxacin was predicted to be mostly immobilized in sludge (75%). These results were consistent with full-scale removal rates reported in literature (refer to [9], [14], [15]). PECs obtained were mostly consistent with MECs, e.g., for the freshwater compartment at local level (Table 1), indicating reliability of the models and of the procedure used. Extension of the two models to not previously tested categories of ionizable compounds (bivalent acid and zwitterion) also proved to be successful. Potential risk was exhibited by triclosan and ciprofloxacin in freshwater (Table 1) and soil compartments (not shown) only at local level. Risk at regional level was found to be negligible, as estimated regional PECs were at most 1 order of magnitude lower than corresponding PNECs. Other risk assessment procedures confirmed the existence of potential risk associated to the release of ciprofloxacin in freshwater ([16], [17]). However, a relevant source of uncertainty was represented by the choice of PNECs from literature, as a wide range of toxicological data was available (e.g., PNEC of triclosan in freshwater ranged from 53 ng/L [11] to 1550 ng/L [12]) and in the case of sediment and seawater compartments PNECs were derived as suggested by REACH guidelines.

Compound – *Scenario*	**PECs**	**MECs**	**Risk quotient**
Triclosan – *Lower Saxony*	80 ng/L	3 – 90 ng/L [8] [9]	1.5 (a), 0.05 (b)
Furosemide – *Denmark*	680 ng/L	250 – 420 ng/L [10]	0.22
Ciprofloxacin – *Northern Italy*	17 - 26 ng/L	25 ng/L [11]	3.4

Table 1. Selected local PECs, MECs and risk quotients in freshwater compartment. For triclosan, (a) refers to risk quotients calculated using PNEC reported by [12], (b) to risk quotients calculated using PNEC reported by [13].

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